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O/W Microemulsions at low surfactant content

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Abstract: Oil-water microemulsions of the five components system water/sodium chloride/toluene/1-butanol/sodium dodecyl sulfate exhibit diffuseness (due to a turbidity gradient) for a very low surfactant content, 0.6 ÷ 0.006 % w/w. The main characteristics of such microemulsions are described and the existence of nonuniformity is discussed.

Key words: Microemulsions with 5 components, water, toluene, 1-butanol, chloride and dodecylsulfate of sodium, Winsor-phases, diffusion effects, influence of temperature.

In this paper we discuss some interesting characteristics of o/w microemulsions, recently investigated [1, 2] for a very low surfactant content (0.6 – 0.006 %), of the five components system: water/sodium chloride/toluene/1-butanol/sodium dodecylsulfate (SDS). Because the aim of the work is a better understanding the role of alcohol, surfactant and temperature in the properties of the amphiphilic compounds, a phase diagram has been determined at constant brine/toluene ratio (≃ 2) and constant salinity (6.5 %); the high salinity value should ensure a practically complete charge screening at the internal interface of the system. The investigation has been carried out in a surfactant concentration range well below that which usually leads to conventional Winsor phases. Under such conditions, a new behavior is exhibited by the samples: transparent upper oily regions coexist with diffuse aqueous regions, the diffuseness being due to a turbidity gradient (see Fig. 1 of Ref. [1]); the interface between the oily and the aqueous regions (which will be simply called 'interface' in the following) is sharp. The phase diagram investigation has been therefore performed to cover the domain for which the new behavior is observed, for different alcohol and surfactant contents and at different temperatures. In Winsor equilibria, a turbid phase of the microemulsion type coexists with an oily phase (Winsor I) or an aqueous phase (Winsor II) or both (Winsor III); the excess phases are always transparent. What distinguishes the samples of this phase diagram from conventional Winsor equilibria is the turbidity gradient of the aqueous domain. This diffuse domain coexists either with transparent oily regions or with turbid intermediate homogeneous regions of microemulsion type, plus transparent oily regions, depending on the parameters' value.

In the five components system under study, an alcohol/surfactant ratio (w/w) higher than 0.9 develops a Winsor III equilibrium and, for a further increase of that ratio (0.9–9), the value of the active mixture percentage necessary to obtain the Winsor III equilibrium decreases [3]. In our phase diagram investigation [2], the alcohol/ surfactant ratio covers the range 4–380, the alcohol and SDS contents are in the range 1.9–2.7 % and 0.006–0.6 %, respectively; for all the samples, the active mixture percentage is 2.8–1.9 % and the investigated thermal range 12 °–30 °C. The aqueous regions exhibit diffuseness for SDS and 1-butanol content in the range 0.006–0.3 % and 1.9–2.5 %, respectively, and for $T = 16$ °–26 °C. An active mixture percentage 2.3–2.8 % and an alcohol/surfactant ratio > 10 are conditions necessary to observe such a diffuseness. We point out that the alcohol content cannot be decreased below 1.9 %, otherwise the surfactant spreads on the interface in the form of a white structure; the 0.006 % SDS content corresponds to the minimum amount still weighted with a good accuracy. For all the samples studied, outside the thermal range in which diffuseness is shown, the aqueous region ex-

hibits a homogeneous turbidity for $T > 26\,°C$, while the surfactant spreads on the interface for $T \leq 16\,°C$ (the two liquid regions separated by the interface are transparent). This last result suggests that, for diffuse samples, the surfactant is close to the solubilization limit, for the given proportions of the other components. In summary, for all the diffuse samples, the brine/toluene ratio is constant and the active mixture percentage is also quite constant; thus, in the pseudoternary phase diagram brine/toluene/active mixture, the mass composition points of the samples are approximately in the same position, while the alcohol/surfactant ratio varies by three orders of magnitude. By a comparison of this phase diagram with that of Ref. [3], the mass composition point of diffuse samples is found to be on the boundary between Winsor I and Winsor III equilibria for the alcohol/surfactant ratio ~ 9.

We should point out that our phase diagram was performed by visual observation on samples thermally stabilized at 0.1 °C for longer than 1 month. This condition could be insufficient to assure the attainment of the thermodynamic equilibrium for samples which are close to the boundary between Winsor I and III equilibria. Thus, the composition and the structure of a typical sample, composed of brine 65.74 %, NaCl salinity 6.5 %, toluene 31.90 %, 1-butanol 2.30 % and SDS 0.04 % (w/w), have been studied with a ± 0.025 °C thermal stabilization over 1 month; the aqueous domain is still diffuse. The composition of the upper region and the average composition of the aqueous domain, as well as the composition profile inside the aqueous domain, have been evaluated by the index of refraction measurements. A direct estimate of the composition of the upper transparent region has been done by gas chromatography. Concerning the structure investigation, the autocorrelation function of the scattered light intensity, $g(t)$ (QELS analysis), has been measured as a function of height throughout the sample. Because the process is diffusive, the mutual diffusion coefficient has been evaluated for all the heights. Furthermore, the transmitted light intensity has been also measured throughout the sample. Variations of the composition and the structure distributions have been observed only during the first stabilization week, thus more than 1 week's stabilization time has been allowed for the sample in all experiments.

We summarize here the main results:

Upper region: No index of refraction variation is observed, thus the upper region is uniform in composition. From the gas chromatographic spectrum, the region is mainly composed of toluene and 1-butanol, in good agreement with the index of refraction results. Furthermore, no correlation time of $g(t)$ is detectable in the limit of resolution of the apparatus and no variation of the transmitted light intensity is observed. This implies that no aggregates of supramolecular size are present there. The upper region results in a homogeneous oily solution, similar to the excess oily phase of Winsor I and III equilibria.

Aqueous Domain: An index of refraction profile indicates a progressive variation of the composition from the interface to the bottom of the domain. Different profiles are obtained for different temperatures in the range 18 °–24 °C. In the aqueous domain, in contrast to the upper region, we detect a correlation time of $g(t)$ for all the investigated heights down to the bottom of the cell. A transmitted light intensity profile is also detected and this profile changes with temperature.

In summary, from the composition and the structure results, we can describe the aqueous domain as composed of three regions: intermediate, diffuse and lower, respectively, from the interface towards the bottom of the sample; the intermediate and the lower regions are uniform in composition and structure, while the diffuse region displays a composition and a structure gradient. The composition and the structure profiles vary with temperature; their trends (they are sharp for $T = 20\,°C$ and $T = 22\,°C$ and smooth for $T = 18\,°C$ and $T = 24\,°C$) agree with the phase diagram observations, despite the better thermal stabilization accuracy of such analyses: in fact, observing with the naked eye, the diffuseness disappears for $T \leq 16\,°C$ and $T > 26\,°C$. Finally, the body of the results allows us to establish that the upper region is an excess oily region, while the aqueous domain is of the o/w microemulsion type, down to the bottom of the cell.

To interpret the nonuniformity of the aqueous domain, a discussion in terms of incomplete phase separation, critical type regime, sedimentation of polydisperse globules due to gravity and globules aggregation has been provided in Ref. [2]. The hypothesis of a critical or precritical regime has been excluded. The diffuse samples relax very slowly after mechanical agitation and are placed on the phase boundaries between two and three phase coexistence domains; thus, a possible explanation for the diffuseness is an incomplete phase separation between the intermediate and the lower regions. Before attaining the studied state (diffuse aqueous region plus transparent oily region), the aqueous domain is a polydisperse emulsion, the concentration gradients being larger than for the studied

state; thus, under the hypothesis of a very slow equilibrium attainment, the tendency is clearly towards a Winsor I equilibrium. However, the sample diffuseness could be linked to a segregation due to gravity of dispersed objects having different sizes, the formation of which could be favoured by the peculiar composition of the sample itself. In this last case the sample should be at equilibrium. To test the hypothesis of a gravity segregation, we have estimated the size of the dispersed objects of the sample intermediate and lower regions. In fact, because the 50 % D variation measured between those regions cannot be interpreted in terms of volume fraction variation at constant size, the $D(h)$ profile suggests the existence of two neighbouring regions with scattering objects of different size (the D value is $0.8 \cdot 10^{-7}$ cm^2/s and $1.3 \cdot 10^{-7}$ cm^2/s for the intermediate and the lower regions, respectively). Assuming that globules are dispersed throughout the aqueous domain, from the mutual diffusion coefficient we can give a rough estimate of a hydrodynamic radius R_H, neglecting corrections due to the finite concentration of the sample, assuming $D \sim D_o$ and simply using the Stokes-Einstein formula; assuming as viscosity that of water wet get $R_H \sim 200$ Å. Moreover, we obtain $R_H = 230$ Å and 160 Å in the intermediate and lower regions, respectively. These values are surely overestimated as the second virial coefficient contribution has been neglected, but the ratio between them (~ 1.5) is presumably correct because of the small volume fraction variation of the dispersed phase between the two regions, $\Delta\phi = 0.0014$. If several sizes coexist by aggregation or curvature fluctuations, in both cases, a sedimentation of large enough globules may arise due to gravity. The competition between Brownian motion and gravity, for samples at equilibrium, gives an exponential distribution $\exp(-\Delta\varrho V\, gh/k_BT)$ with $\Delta\varrho =$ density difference between the continuous and the dispersed phase, where V is the droplet volume and g the gravity accelearation; the characteristic length scale over which sedimentation occurs is $l = k_BT/\Delta\varrho Vg$. In our case, supposing the sample at equilibrium, we get $l = 18$ cm for $R = 160$ Å, and $l = 6$ cm for $R = 230$ Å. The size distribution should thus vary with h, larger globules sedimenting towards the oil-microemulsion interface. Of course, a sum of two exponential decays should give a monotonic decreasing function; thus, a gravity segregation of globules of two different sizes cannot explain the whole trend of the profiles. Furthermore, no significant polydispersity has been found in QELS experiments, therefore we cannot deduce a featuring size distribution of the globules. The main question about the origin of the diffuseness remains not fully answered. However, it can be demonstrated that a microemulsion is obtained down to a very low surfactant content. Furthermore, the microemulsion interfacial film appears to be very rich in alcohol. An indirect estimation of the interfacial film composition can be obtained as follows. Since under reasonable hypotheses the average volume fraction of the dispersed phase and the average hydrodynamic radius have been evaluated, the composition and the structure results can be compared by means of the formula $R = 3\phi/n_s\Sigma$ where R is the average radius of the globules, n_s the number of surfactant molecules per unit volume and Σ the area per surfactant molecule of the interfacial film ($\Sigma \simeq 60$ Å^2) [4]. Usually the Σ value is related to one surfactant molecule plus one alcohol molecule; however, in the present case, using as R and ϕ values of 200 Å and 0.0275, respectively, the number of alcohol molecules per surfactant molecule at the interface of the microemulsion is ~ 20, one order of magnitude higher than usual. Such an alcohol-rich film is expected to present peculiar mechanical characteristics corresponding to a quite low rigidity coefficient (K) of the interface which could favor strong curvature fluctuations leading to polydispersity or aggregation. We recall that the aqueous domain loses its diffuseness for $T \leq 16$ °C and for $T > 26$ °C. For $T \leq 16$ °C the aqueous domain is perfectly transparent; probably the curvature energy is too high, with respect to thermal energy ($K > K_BT$), to give a dispersion of microemulsion type. For $T > 26$ °C the aqueous domain is turbid homogeneous; the thermal energy seems to prevail ($K < K_BT$) and such a dispersion is favored. Thus, for intermediate temperatures, an intermediate case is expected: the competition between rigidity and thermal energy could favor large curvature fluctuations, therefore the coexistence of dimetric, trimeric . . . aggregates can be justified, as well as the coexistence of globules of different size. At the present stage of measurements we have no information on the shape of the globules. The 1.5 ratio between the diameters of the globules of the intermediate and lower regions could support the hypothesis of an intermediate region mainly composed of oily dimeric aggregates.

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